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Global and Local Influences on the Chemical Composition of Snowfall  
at Dye 3 Greenland: the Record Between 10 kaBP and 40 kaBP

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Abstract

Wisconsin Age ice from Dye 3, Greenland, shows a number of  $\delta^{18}\text{O}$  level-changes which indicate the occurrence of rapid climate transitions. In order to study the effect of climate change on geochemical fluxes we have selected several of these transitions for chemical analysis. At each transition we have measured chloride, nitrate and sulfate concentrations with 5 cm depth resolution. All three anionic species show significant variations which correlate with the measured  $\delta^{18}\text{O}$  shifts. In general, periods of high  $\delta^{18}\text{O}$  (warm periods) have lower anion concentrations than adjacent periods of low  $\delta^{18}\text{O}$  (cold periods). However, the relative concentration shifts are not the same for all species, indicating that the concentration variations cannot be caused only by changes in snow accumulation rate acting on a constant anion flux. In addition to these rapid concentration changes, over the last 40 ka slower, secular variations in baseline concentrations also occurred. Baseline chloride and sulfate concentrations reached maxima near time of maximum ice volume. Baseline nitrate, on the other hand, remained relatively constant until near the end of the glaciation when its concentration rose. If a constant sulfate flux is assumed, the measured sulfate concentrations imply a dependence of snow accumulation rate on  $\delta^{18}\text{O}$  for the Wisconsin which is similar to that presently observed in Greenland. The sulfate concentrations would then suggest that Wisconsin snowfall rates were, at times, as much as eight times lower than today.

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## Introduction

The value of polar ice sheets as archives of paleo-environmental conditions has been impressively demonstrated by studies of  $\delta^{18}\text{O}$  [1,2] and  $\text{CO}_2$  [3,4] in the Greenland and Antarctic ice sheets. The  $\delta^{18}\text{O}$  of ice gives a more or less direct indication of climate conditions at the time of deposition [1]. Although it is often convenient to interpret high  $\delta^{18}\text{O}$  as representing warm conditions and low  $\delta^{18}\text{O}$  cold conditions, oxygen isotope ratios are influenced by a range of parameters, which includes, in addition to temperature, ice sheet elevation, distance to the water vapor source and isotope ratio in the source. Therefore, when using  $\delta^{18}\text{O}$  as a climatic indicator, climate must be understood in very general terms. The relation between  $\text{CO}_2$  and climate is less clear cut than for  $\delta^{18}\text{O}$ . However, measurements have shown the  $\text{CO}_2$  content of polar ice to be high during periods of high  $\delta^{18}\text{O}$  ("warm" periods) and low during periods of low  $\delta^{18}\text{O}$  ("cold" periods) [6]. If the change in the  $\text{CO}_2$  concentration in polar ice is climate-related, it may reflect changes in biological productivity, as has been proposed [5]. Then we might also expect to see changes in the geochemical fluxes of species besides carbon which are biologically influenced. In order to investigate this hypothesis, and the general relation between climate and atmospheric chemistry, we have measured chloride, nitrate and sulfate concentrations in selected stratigraphic intervals of the Dye 3 deep ice core in which significant  $\delta^{18}\text{O}$  variations also exist.

Herron & Langway [7] have already reported that a marked decrease in anion concentration at Dye 3 accompanied the warming at about 10 kaBP which terminated the Wisconsin glaciation. Our results show in addition, that during the Wisconsin, chloride, nitrate and sulfate concentrations at Dye 3 changed significantly at several other periods of rapid climate fluctuation and further, that the concentrations of these species have shown long-term secular variations extending over the last 35 ka to 40 ka.

## Experimental

Samples for this study were obtained from the 2037 m Dye 3 ( $65.18^\circ\text{N}$ ,  $43.83^\circ\text{W}$ ) (Figure 1) ice core drilled in Greenland between 1979 and 1981 during field operations associated with the American-Swiss-Danish Greenland Ice Sheet Program (GISP). Core samples were cut in the laboratory at 5 cm depth intervals in a  $-15^\circ\text{C}$  cold room using a bandsaw. This cutting interval ensures that all samples include precipitation from several years and therefore that seasonal variations in precipitation chemistry are averaged out. The samples, weighing between 40 g and 50 g, were cleaned with acetone

(to remove any traces of drilling fluid) and ultrapure water (18 Mohm-cm) in a class 100 clean room. The cleaned samples were placed in polypropylene cups which had been pre-cleaned by soaking in ultrapure water, and were melted in a microwave oven. Chloride, nitrate and sulfate analyses were carried out with a Dionex Model 10 ion chromatograph. A ten gram aliquot of melted ice water was injected onto a Dionex AG-3 concentrator column and then eluted from a Dionex AS-3 separator column with a mixture of 2.70 mM  $\text{Na}_2\text{CO}_3$  and 1.35 mM  $\text{NaHCO}_3$ . Concentrations were determined by comparing peak heights with those of fresh standards measured during each analytical run. Blank values ( $\text{Cl}^- = 1$  ppb,  $\text{NO}_3^- = 3$  ppb,  $\text{SO}_4^{2-} = 1$  ppb) were determined by processing frozen ultrapure laboratory water in the same manner as the actual ice samples. The measured concentrations were not corrected for the blanks. The one standard deviation uncertainty, determined from the standards, is about 7% for the concentrations found in the samples.

## Results

In order to investigate the relation between climate (as indicated by  $\delta^{18}\text{O}$ ) and chemical composition, we chose for analysis four depth zones in the Dye 3 core at which significant  $\delta^{18}\text{O}$  perturbations were observed. The approximate ages of these depth zones, calculated using the model age relations of Dansgaard et al. [8], are: 1809-1813 m = 15 kaBP, 1845-1849 m = 25 kaBP, 1866-1870 m = 30 kaBP and 1879-1888 m = 35 kaBP. Figure 2 summarizes all available chemical data between 1784 m and 1888 m, as well as  $\delta^{18}\text{O}$  results for the same regions [Dansgaard et al., personal communication]. In Figure 3 chloride, nitrate, total-sulfate and  $\delta^{18}\text{O}$  data are plotted on an expanded scale, for selected stratigraphic zones, to illustrate the correlations between parameters.

The first observation which can be made from the data in Figure 3 is that during periods of higher  $\delta^{18}\text{O}$  the concentration of all measured anionic species decreased, but not in each case by the same factor. The second observation is that although each of the  $\delta^{18}\text{O}$  shifts which we investigated was accompanied by a change in chemical concentration, the initial changes in composition, especially for sulfate, tended to stratigraphically precede the  $\delta^{18}\text{O}$  changes. This observation reinforces the conclusions of Dansgaard et al. [9] that the oxygen isotope excursions represent actual environmental changes and not stratigraphic discontinuities or folding. Relative changes in sulfate concentration are always larger than corresponding changes in nitrate and chloride. Our data are summarized in Table 1 which shows that at various times in the past with approximately similar  $\Delta\delta^{18}\text{O}$  the relative changes in nitrate and sulfate concentration have been approximately constant while the temperature dependence of chloride has increased.

## Sources

Chloride, nitrate and sulfate each have different sources in Greenland snow.

-Chloride in the unpolluted atmosphere originates primarily as sea spray entrained by oceanic winds. Volcanic eruptions constitute a second, transient source which can greatly increase the chloride content above baseline levels for brief periods [10].

-Nitrate in the atmosphere has a complex source which is still poorly understood. The global nitrate budget has recently been reviewed by Logan [11]. The important precursors of nitrate are NO and NO<sub>2</sub> which are lumped together as NO<sub>x</sub> because they rapidly equilibrate with each other through photochemical reactions in the atmosphere. Direct emission of NO, production by lightning, oxidation of NH<sub>3</sub> and transfer from the stratosphere predominate in the sources of NO<sub>x</sub> [11,12,13]. In the troposphere, NO<sub>x</sub> is oxidized to HNO<sub>3</sub>, which constitutes the primary sink of atmospheric nitrogen oxides.

-Sulfate originates through the activities of marine and terrestrial organisms which produce volatile reduced sulfur species that become oxidized to sulfate in the atmosphere. Recent work [14,15] has emphasized the importance of the marine source of (CH<sub>3</sub>)<sub>2</sub>S. Sulfate, in addition, has two other important sources (see [16] for a recent estimate of global sulfate fluxes). First, like chloride, it originates over the ocean as entrained sea spray, with a SO<sub>4</sub><sup>2-</sup>/Cl<sup>-</sup> mass ratio of about 0.14. In this paper, sulfate concentrations which have been corrected by subtracting 0.14 times the chloride concentration are termed excess-sulfate. Secondly, volcanic emanation may constitute a significant source of atmospheric sulfur and following violent eruptions may lead to significant transient increases in the sulfate concentration of snowfall [17].

It is probably not correct to interpret Greenland fluxes as representative of global geochemical cycles for chlorine, nitrogen and sulfur. As shown below, the flux (mg/m<sup>2</sup>y) in Greenland of chloride and sulfate is less than 5% of the non-anthropogenic global atmospheric flux. Even in the case of nitrate, the Greenland flux is less than 25% of the global average. It will therefore be necessary to consider regional sub-cycles in order to understand the Greenland deposition pattern.

## Present-day Deposition

The relation between meteorological conditions and snow chemistry in recent Greenland deposits provides information about the geochemical system active in Greenland which can serve as a basis for interpreting the Wisconsin Age data. Herron [17] has reported average chemical compositions at several stations in Greenland for geologically recent, pre-industrialized times and concluded that for  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  accumulation rate is the controlling variable while for  $\text{Cl}^-$  elevation seems to predominate in controlling average concentrations. In order to compare recent data with Wisconsin Age results where accumulation rates and elevations are not known, we have replotted the data, in terms of both concentration and flux, as a function of  $\delta^{18}\text{O}$ . Since there is a strong correlation between  $\delta^{18}\text{O}$  and accumulation rate in Greenland, it is not surprising that we find similar trends to those observed by Herron [17] for  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ . These data are replotted in Figure 4 as both concentrations and fluxes. The temperature and accumulation rate for each site are shown on Figure 1 and range from  $-32^\circ\text{C}$  and 0.10 m.w.e. (meters water equivalent) at North Central to  $-20^\circ\text{C}$  and 0.50 m.w.e. at Dye 3. Both nitrate and excess-sulfate concentrations increase with decreasing temperature, while chloride is approximately constant as a function of temperature. These results contrast with our Wisconsin data which shows that at Dye 3  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  concentrations all increased during periods of low  $\delta^{18}\text{O}$ .

Further insight into the significance of these patterns can be had by examining the flux variations in addition to the concentration variations. For recent samples it is possible to determine snow accumulation rates by counting annual layers in  $\delta^{18}\text{O}$ . This information then allows calculation of deposition fluxes. In the case of chloride, the data clusters into two groupings. Dye 3, Milcent and Camp Century have high chloride fluxes. These three stations are below 2500 m in elevation and exhibit a stronger marine influence than the other two stations, Crete and North Central, which are further inland or at a higher elevation, above 2500 m, and have lower chloride fluxes. Chloride fluxes seem to provide an indicator of marine influence [26]. Measured chloride fluxes in Greenland range between 5 and 15  $\text{mg Cl/m}^2\text{y}$ , which is only a few percent of the estimated global average atmospheric input of 600  $\text{mg Cl/m}^2\text{y}$  [10].

The measured  $\text{NO}_3^-$  flux in Greenland varies between about 2 and 6  $\text{mg N/m}^2\text{y}$ , which can be compared with an estimated mean global flux to the atmosphere of 27  $\text{mg N/m}^2\text{y}$  [11,13]. The nitrate flux correlates positively with higher  $\delta^{18}\text{O}$ . In general, snow accumulation rates decrease as a function of temperature in Greenland much faster than the nitrate concentration increases, so that a cold site such as North Central has a much lower flux



than a warm site such as Dye 3, even though the nitrate concentration is significantly higher at North Central.

Our knowledge of detailed source strengths, pathways and deposition mechanisms for nitrate in Greenland is still too sketchy to allow us to decide which of the possible mechanisms which can be invoked to explain this pattern are actually responsible. However, a clue may be found in the distinct summer nitrate maximum observed at Dye 3 during the Holocene. Summer nitrate concentrations are a factor of 5 or more greater than winter values [17, 27]. Similar summer nitrate peaks have been observed at other sites in Greenland and the Antarctic [19,20]. There are several possible explanations for the summer nitrate peak: 1.) The elevated summer nitrate levels may reflect increased photochemical production of  $\text{HNO}_3$ . 2.) They may indicate that during the summer, when the polar front is farther to the north [25], circulation patterns tend to bring more southerly air to Greenland, producing a corresponding increase in the air concentration of either  $\text{NO}_x$  or of nitrate itself. 3.) The fact that nuclear fallout species show a similar elevated concentration in summer precipitation [21] may indicate that stratospheric nitrate contributes significantly to the summer nitrate budget. Hameed et al. [18] and Risbo et al. [19] have discussed evidence for a stratospheric source of nitrate. Any of these mechanisms or a combination may be acting. For example, summer nitrate may result from the transport of mid-latitude air masses, but the ultimate source could still be stratospheric. It could also be lightning [18,22] or a flux of biogenic reduced nitrogen. Both sources are expected to show a warm season maximum. The possible importance of a biogenic source is supported by the lower nitrate flux in the land-poor southern hemisphere, as determined in Antarctic ice samples from stations with similar temperatures to those where the Greenland measurements were made [17]. On the other hand,  $^7\text{Be}$  measurements [18] suggest that stratosphere-troposphere exchange may be as much as a factor of two less important in the southern hemisphere than in the northern, a fact which would permit the Antarctic data to be consistent with a stratospheric source of nitrate.

The systematics of the geographical distribution of nitrate fluxes in Greenland provides information complementary to the seasonal data. The higher nitrate fluxes at warmer stations such as Milcent and Dye 3 could reflect the presence of mid-latitude air masses whose increased  $\text{NO}_x$  content, of either stratospheric, biogenic or lightning origin, could potentially offset the diluting effects of increased snowfall rates. On the other hand, the lower nitrate fluxes at colder stations such as North Central and Crete shown in Figure 4 do not necessarily reflect a decreased mid-latitude input. These colder sites are also higher in altitude and may be sampling upper altitude air masses which have not been as strongly effected by scavenging

as the warmer stations which are at lower altitudes.

The sulfate flux in Greenland shows only a slight temperature dependence, with an approximately constant excess-sulfate value of 3 mg S/m<sup>2</sup>y. This flux can be compared with a global average non-seasalt atmospheric input of more than 230 mg S/m<sup>2</sup>y [16]. The uniformity of the observed flux suggests the dominance of a diffuse source for sulfate in Greenland, which is in agreement with recent studies [14,15] which show the importance of the marine biogenic flux of (CH<sub>3</sub>)<sub>2</sub>S in the global sulfate budget. Such a diffuse biogenic source could provide a relatively constant concentration of sulfate precursor in the atmosphere which would be consistent with the uniform flux observed. The difference between the pattern for sulfate and chloride may derive from the different size distribution of the chloride and sulfate aerosol particles. The size distribution of marine chloride aerosol peaks at a greater diameter than that of sulfate [28]. Chloride aerosol therefore more readily forms condensation nuclei than sulfate and has a shorter atmospheric residence time. Sulfate aerosol is transported further and at higher altitude than chloride.

#### Wisconsin Deposition

By extrapolating from this pattern of recent deposition we can now try to understand the Wisconsin variations which are shown in Figures 2 and 3. It can be asked whether the changes in anion concentration are due to changes in the global source strengths and transport pathways for these species or whether they are instead due to changes in local deposition mechanisms acting in an environment of constant atmospheric concentration. The consistent decrease to lower anion impurity concentration when  $\delta^{18}O$  increases suggests that a dominating factor controlling the systematic variations visible in Figure 2 and in Table 1 is a change in precipitation rate. Warmer air has a higher water vapor capacity than cooler air and can therefore produce higher precipitation rates on cooling. Such an increase in precipitation rate, acting on a constant source strength of impurity, would result in a decrease in concentration in the snow. However, as has already been pointed out, the relative change in concentration was not the same for each chemical species. The cause therefore, cannot be simply a dilution of a constant chemical flux by a higher snowfall rate during warmer periods.

Of the three species measured, the sulfate concentrations in Wisconsin ice from Dye 3 show the greatest change as a function of temperature. For a  $\delta^{18}O$  increase of about 4‰ (which, assuming the same relationship between  $\delta^{18}O$  and temperature as today, would correspond to a temperature change of about 6°C [1]), the SO<sub>4</sub><sup>2-</sup> concentration decreases by about a factor of

four. The uniformity (to within 25%) of the pre-industrial (Holocene) excess-sulfate flux over Greenland (Fig. 4) suggests that this parameter is dominated by a diffuse and constant source which is little influenced by regional differences in meteorology. As a first pass at explaining the Wisconsin observations we have investigated the consequences of assuming, as suggested by Herron [17], that the recent near constancy of the sulfate flux, and the resulting inverse proportionality between sulfate concentration and snow accumulation rate, also held during the Wisconsin. We can examine the validity of this assumption over both long and short time scales. In view of the drastic climatic changes which occurred, it might seem unlikely that the sulfate flux in Greenland has remained constant for the last 40 ka. It would be less surprising if sulfate fluxes had remained constant over the 100 - 200 years required for the late Wisconsin  $\delta^{18}\text{O}$  transitions to occur. In fact, Table 1 shows that at these transitions the cold/warm excess-sulfate concentration ratio remained constant at about 4 for the roughly equal  $\delta^{18}\text{O}$  shifts of around 4‰. At least over the short times spanned by these transitions, it is thus plausible to attribute the change in sulfate concentration to a change in snowfall rate of about a factor of four.

Although the long-term constancy of the sulfate flux is much more suspect than the short-term constancy, we can, by assuming that the flux of excess-sulfate at Dye 3 has been equal to today's level of  $10 \text{ mg SO}_4^{2-}/\text{m}^2\text{y}$  since 40 kaBP, use measured sulfate concentrations to infer snow accumulation rates during Wisconsin times. We have used the measured  $\text{SO}_4^{2-}$  concentrations immediately before and after the rapid cold-warm transitions (given in Table 1) to calculate accumulation rates. In Figure 5 we have plotted the resulting calculated accumulation rates against  $\delta^{18}\text{O}$  during the Wisconsin. On the same figure we have also plotted measured present-day accumulation rates at various Greenland stations. The correlation between accumulation rate and  $\delta^{18}\text{O}$  (temperature) is quite good (correlation coefficient = 0.92). Surprisingly, although there is some scatter in the data, sulfate concentrations seem to give a consistent estimate of snow accumulation rates in Greenland. These results indicate that during cold periods the accumulation rate may have been, at times, as much as a factor of eight lower than at present, while warm period fluxes were 75%-80% of current values.

A second possibility for explaining the change in sulfate concentrations is that changing climatic conditions influenced the source strength of biogenic reduced sulfur. The decreases in atmospheric  $\text{CO}_2$  content have been related to increases in the flux of carbonate into the deep ocean induced by higher biological productivity in the mixed layer [5,23]. The concomitant higher metabolic activities could also be expected

to produce more  $(\text{CH}_3)_2\text{S}$  [14,15] which upon oxidation could result in a higher sulfate flux in Greenland. Or, alternatively, an extended period of high volcanic activity could also have led to higher  $\text{SO}_4^{2-}$  concentrations or the increased microparticle content [9] may signal a more active particulate source of sulfate during the cold periods. We cannot as yet definitely distinguish between these possibilities. However, the rather good agreement of the calculated relationship between snowfall rate and  $\delta^{18}\text{O}$  for the Wisconsin with that measured for recent times leads us to prefer the accumulation rate explanation at the moment.

Like sulfate, nitrate concentrations are inversely correlated with temperature. However, whereas sulfate increases by a factor of four for a  $\Delta\delta^{18}\text{O}$  of about 4‰,  $\text{NO}_3^-$  increases only by a factor of 1.4. The measured  $\text{NO}_3^-$  concentration and  $\delta^{18}\text{O}$  values for present-day Greenland snowfall show that a change of  $\delta^{18}\text{O}$  from -31.5‰ to -35.5‰, similar to that which occurred during the Wisconsin transitions, would correspond to a relative nitrate concentration increase of 1.3. Nitrate in recent snowfall, therefore, exhibits the same attenuated temperature response, relative to sulfate, that it does in Wisconsin snowfall, although it must be held in mind that the recent pattern is geographically controlled while the Wisconsin pattern is temporally controlled.

Unlike sulfate and nitrate, the Wisconsin chloride deposition pattern differs from that of the present day. Chloride concentrations in the Wisconsin showed a definite dependence on temperature similar to that of nitrate, cold periods having higher concentrations than warm periods. This may imply that a marine component was of greater importance during cold periods than during warm and may indicate that wind velocities were higher during the Wisconsin cold periods or that a more southerly position of the polar front resulted in drier conditions and concomitantly less efficient scavenging of aerosols during transport.

### Secular Trends

In Figure 2 are plotted  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and excess-sulfate concentrations between 1784 m and 1888 m, i.e. between 10 kaBP and about 40 kaBP. In addition to the wide range of concentrations visible at each depth interval, a range which reflects the temperature dependences which have been discussed above, there are clear secular trends in baseline concentration extending over the entire time period between 10 kaBP and 40 kaBP. During this period, warm-epoch excess-sulfate concentrations tend to be approximately constant (20-30 ppb) except at about 1847 m, while cold-epoch sulfate values reach a maximum around 1853 m. Baseline nitrate concentrations tended to

remain constant until about 1810 m (14 kaBP) after which values rose. The chloride pattern is similar to that of sulfate. If we accept the assumption that sulfate concentrations directly reflect snow accumulation rates (and use the Dansgaard et al. time scale [8]) then these trends suggest the following geochemical scenario. Around 1880 m (35 kaBP) snow accumulation rates were similar to those just before the end of the Wisconsin. The sulfate flux, being dominated by a climatically more stable marine source, was similar to that of today. A larger meridional temperature gradient than today produced increased windstress in open ocean areas which caused higher atmospheric chloride concentrations than today. Nitrate concentrations were low, but showed a similar temperature dependence as today. After 1860 m (30 kaBP) accumulation rates decreased to a minimum and chloride and sulfate concentrations reached maximum values. Nitrate values remained low, perhaps because of the continued low level of terrestrial micro-organism activity. Then the snow accumulation rate again increased. By 1810 m (14 kaBP), nitrate levels had begun to rise indicating an increase in mid-latitude biological activity. An alternate explanation for the nitrate increase in the Holocene, namely a change in global atmospheric circulation which led to a larger input of a stratospheric nitrate component or increased input of southerly air, is not indicated by the  $^{10}\text{Be}$  [24] results which show generally lower Holocene than Wisconsin concentrations.

This scenario is open to extensive modification as more information becomes available. One must, for example, consider the possible influence of increased volcanism during the Wisconsin which, through an input of aerosols, could have had the combined effect of elevating chloride and sulfate concentrations and lowering temperatures. It is also possible that high sulfate concentrations during the Wisconsin are partially caused by increased marine metabolic activity. And the effect of sea ice both on  $\delta^{18}\text{O}$  and on chloride concentrations needs to be studied further. Present data does not allow us to differentiate among these three factors.

## Conclusions

This study has shown that chloride, nitrate and sulfate concentrations measured in Wisconsin ice from Dye 3, Greenland show significant concentration variations which correlate with measured  $\delta^{18}\text{O}$  shifts. In general, periods of high  $\delta^{18}\text{O}$  (warm periods) have lower anion concentrations than periods of low  $\delta^{18}\text{O}$  (cold periods). Furthermore, the relative concentration shifts are not the same for all species. This observation implies that the variations are not the result of a simple dilution of a constant impurity flux by a variable snow accumulation rate. The temperature dependence of anion fluxes in Wisconsin Age Greenland snow reflects changes

in source functions, deposition mechanisms and transport processes. It was also derived that the assumption of a constant sulfate flux, although certainly open to question, implies a  $\delta^{18}\text{O}$  dependence of accumulation rate for the Wisconsin which is consistent with that observed today and suggests snowfall rates at times as much as eight times lower during the Wisconsin. In conclusion we deduced that secular variations in concentrations over the last 40 ka show that chloride and sulfate reached concentration maxima near time of maximum ice volume. Nitrate, on the other hand, remained relatively constant until near the end of the glaciation when its concentration rose.

The question of biospheric influence, which motivated this study, remains unanswered. Nitrate and sulfate concentrations show variations which could be caused by changes in biological activity, but which might also result from changes in atmospheric mixing or from changes in parameters which control the mechanism by which atmospheric impurities are incorporated in snow.

Future studies of chemical fluxes in both Greenland and the Antarctic and, for elucidating  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  pathways, stable N and S isotope analyses, will be able to help differentiate among these possible mechanisms.

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## Figure Captions

Figure 1 Location map of various ice core drilling sites in Greenland.

Figure 2 Chloride, nitrate and total-sulfate concentrations during the Wisconsin measured in the Dye 3 ice core. The data above 1884 m are from [7].  $\delta^{18}\text{O}$  data have been kindly provided by W. Dansgaard and his co-workers.

Figure 3 Chloride, nitrate and total-sulfate concentrations as a function of depth measured in the Dye 3 deep ice core during selected intervals where  $\delta^{18}\text{O}$  indicates a rapid climate change.  $\delta^{18}\text{O}$  data have been kindly provided by W. Dansgaard and his coworkers.

Figure 4 Concentrations and fluxes of anions at the five sites in Greenland shown in Figure 1. All concentrations and fluxes are in terms of the anionic species plotted. Sulfate values are excess sulfate. Chemical data is replotted from tables and figures in [17]. Milcent data is from [Herron, unpublished results]. NC=North Central, C=Crete, CC=Camp Century, MC=Milcent, D3=Dye 3.

Figure 5 Snow accumulation rates as a function of  $\delta^{18}\text{O}$ . Open Circles are accumulation rates for Wisconsin deposition at Dye 3 calculated by assuming a constant sulfate flux (see text). Triangles indicate the five sites shown in Figure 1. Symbols are the same as in Figure 4.

### Table Caption

Table 1 This table summarizes some of the chemical data presented in Figure 2. Average chloride, nitrate and excess-sulfate concentrations compositions at five depths in the Dye 3 core where rapid  $\delta^{18}\text{O}$  excursions were observed have been calculated for the period immediately preceding and immediately following the transitions. These mean values are given in columns 2 and 3 at each depth. Column 4 gives  $\Delta$ , the change in  $\delta^{18}\text{O}$  at the transition, and R, the cold-to-warm ratio in chemical composition. The last row at each depth gives  $\lambda_{\text{sulf}}$ , the snow accumulation rate in m.w.e., calculated by assuming a constant sulfate flux (see text). For comparison, recent average compositions for two sites in Greenland are given at the end of the table. The data for 1787 m are from [7].

Table 1

1787 m				1812 m			
	cold	warm			warm	cold	
$\delta^{18}\text{O}(\text{‰})$	-35.7	-31.0	$\Delta=4.8$	$\delta^{18}\text{O}(\text{‰})$	-33.6	-29.9	$\Delta=3.7$
$\text{Cl}^-(\text{ng/g})$	60	25	$R=2.4$	$\text{Cl}^-(\text{ng/g})$	65	35	$R=1.9$
$\text{NO}_3^-$	75	50	1.5	$\text{NO}_3^-$	50	35	1.4
$\text{SO}_4^{2-}$	72	21	3.4	$\text{SO}_4^{2-}$	101	25	4.0
$\lambda_{\text{sulf}}$	.14	.48		$\lambda_{\text{sulf}}$	.10	.40	

1846 m				1867 m			
	cold	warm			cold	warm	
$\delta^{18}\text{O}(\text{‰})$	-35.6	-31.8	$\Delta=3.8$	$\delta^{18}\text{O}(\text{‰})$	-35.4	-32.5	$\Delta=2.9$
$\text{Cl}^-(\text{ng/g})$	95	70	$R=1.4$	$\text{Cl}^-(\text{ng/g})$	75	60	$R=1.3$
$\text{NO}_3^-$	35	25	1.4	$\text{NO}_3^-$	45	30	1.5
$\text{SO}_4^{2-}$	167	35	4.8	$\text{SO}_4^{2-}$	150	32	4.7
$\lambda_{\text{sulf}}$	.06	.29		$\lambda_{\text{sulf}}$	.07	.31	

1880 m			
	cold	warm	
$\delta^{18}\text{O}(\text{‰})$	-35.6	-31.5	$\Delta=4.1$
$\text{Cl}^-(\text{ng/g})$	75	50	$R=1.5$
$\text{NO}_3^-$	45	30	1.5
$\text{SO}_4^{2-}$	110	23	4.8
$\lambda_{\text{sulf}}$	.09	.43	

Recent		
	Dye 3	North Central
$\delta^{18}\text{O}(\text{‰})$	-27.8	-35.8
$\text{Cl}^-(\text{ng/g})$	23	27
$\text{NO}_3^-$	50	83
$\text{SO}_4^{2-}$	20	76

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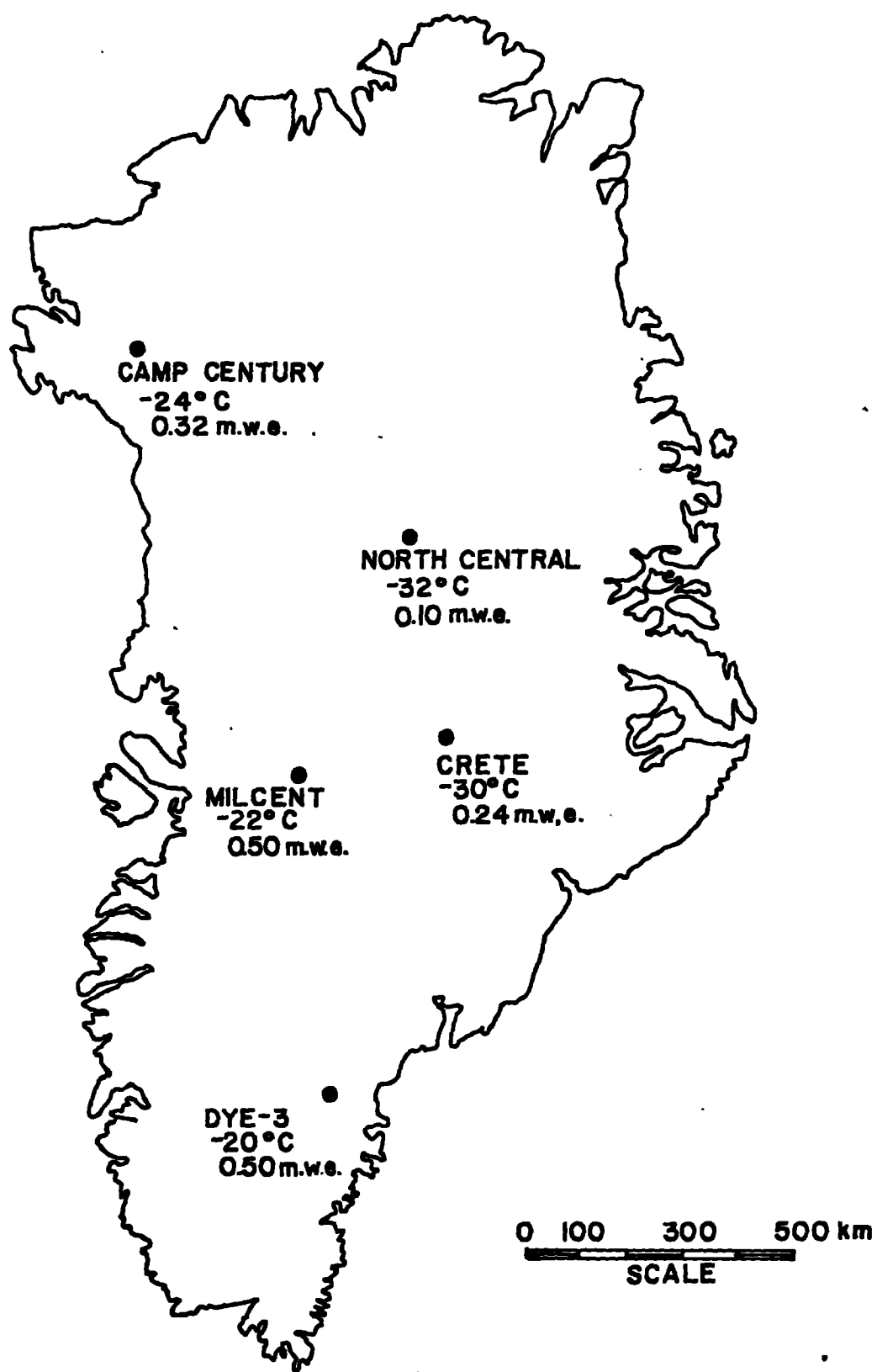


FIGURE 1.

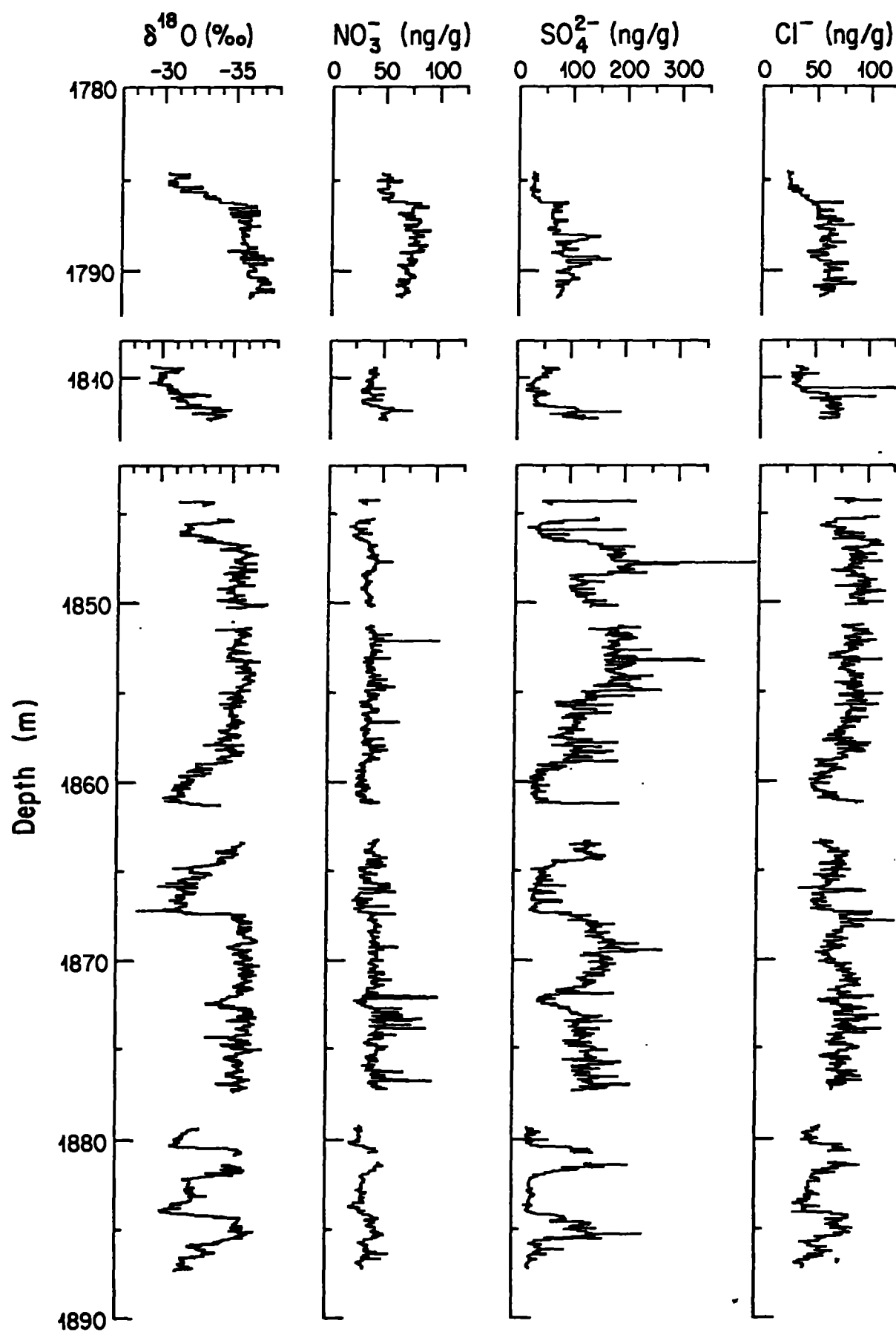


FIGURE 2.

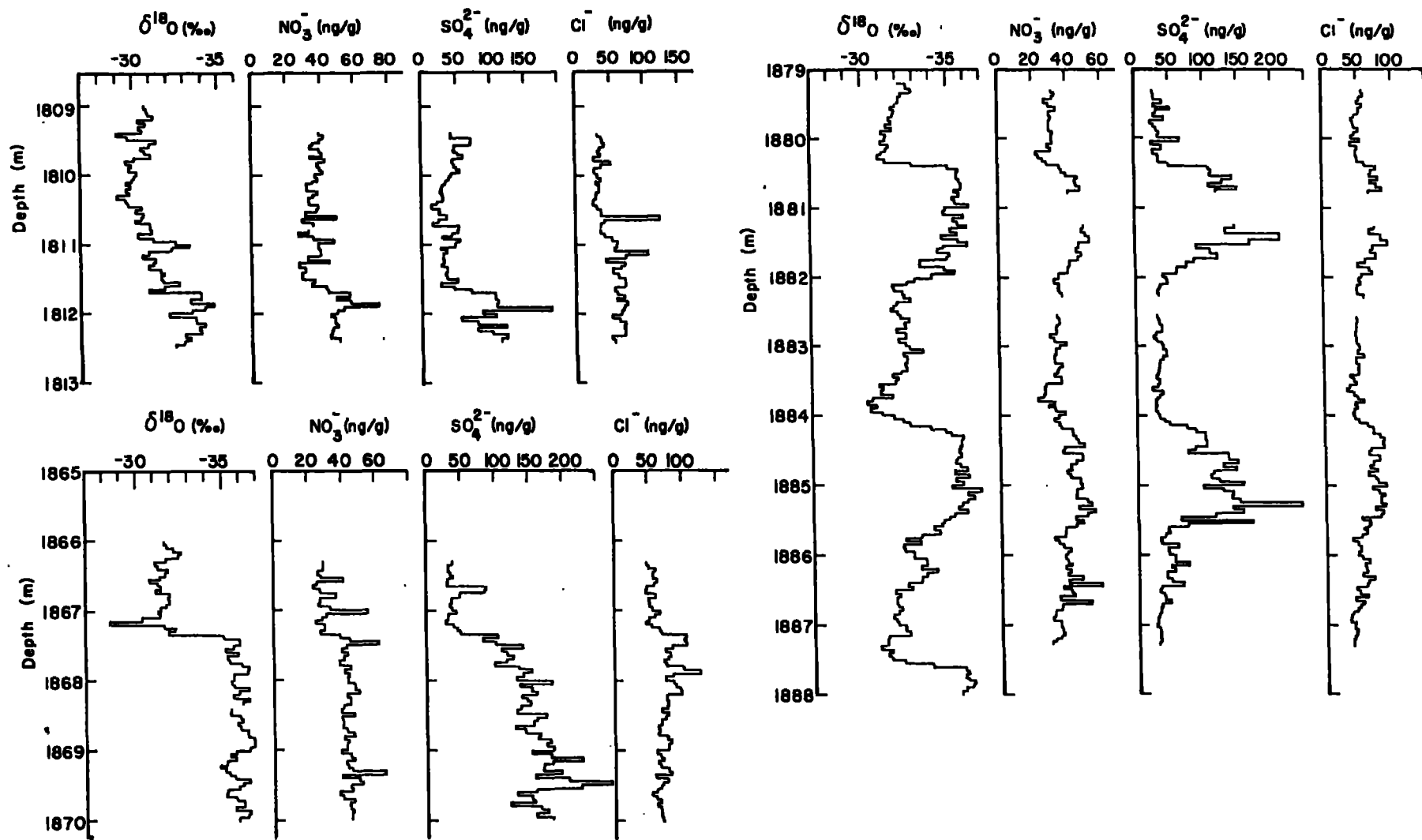


FIGURE 3.



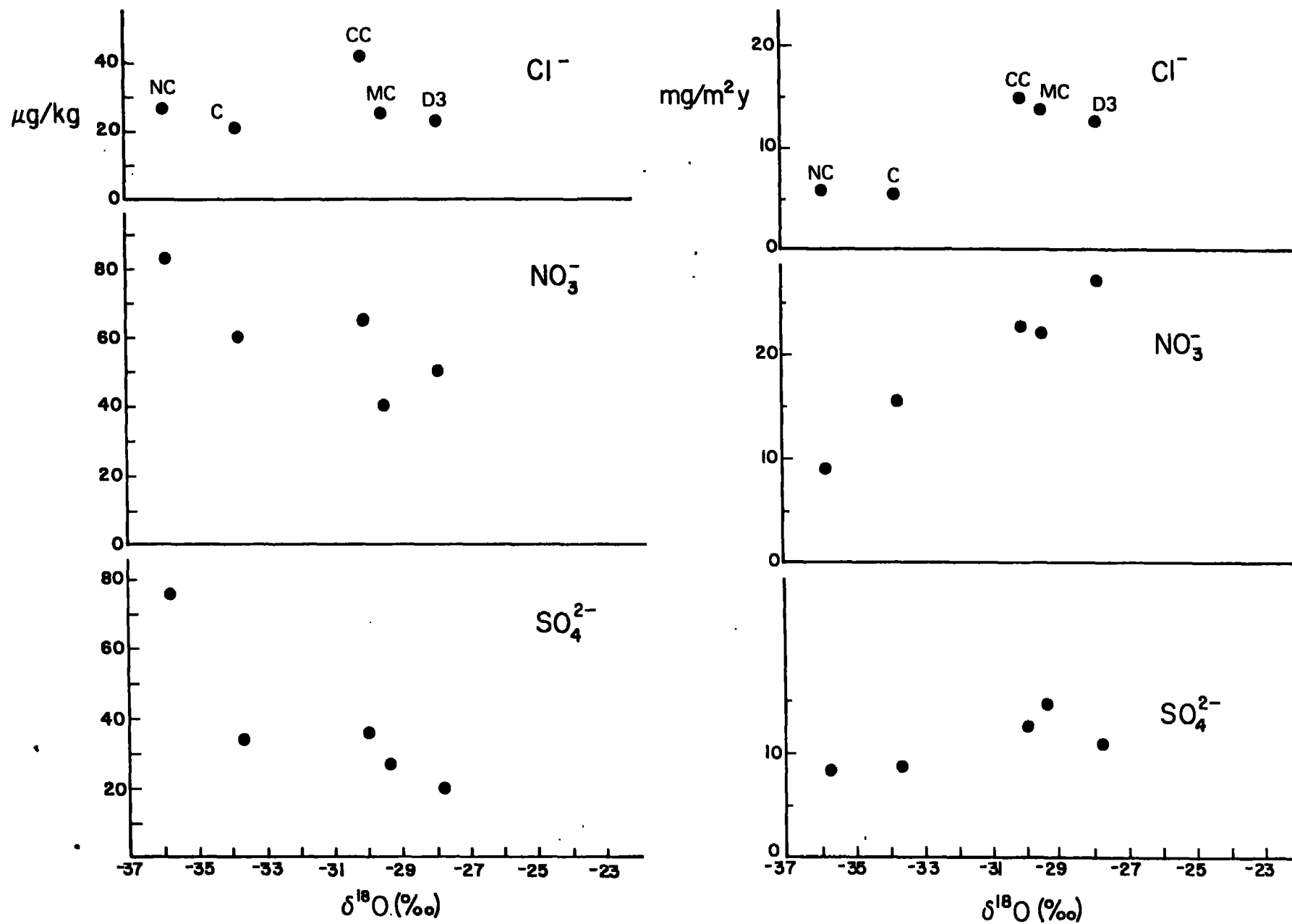


FIGURE 4.

# Accumulation Rate vs $\delta^{18}\text{O}$

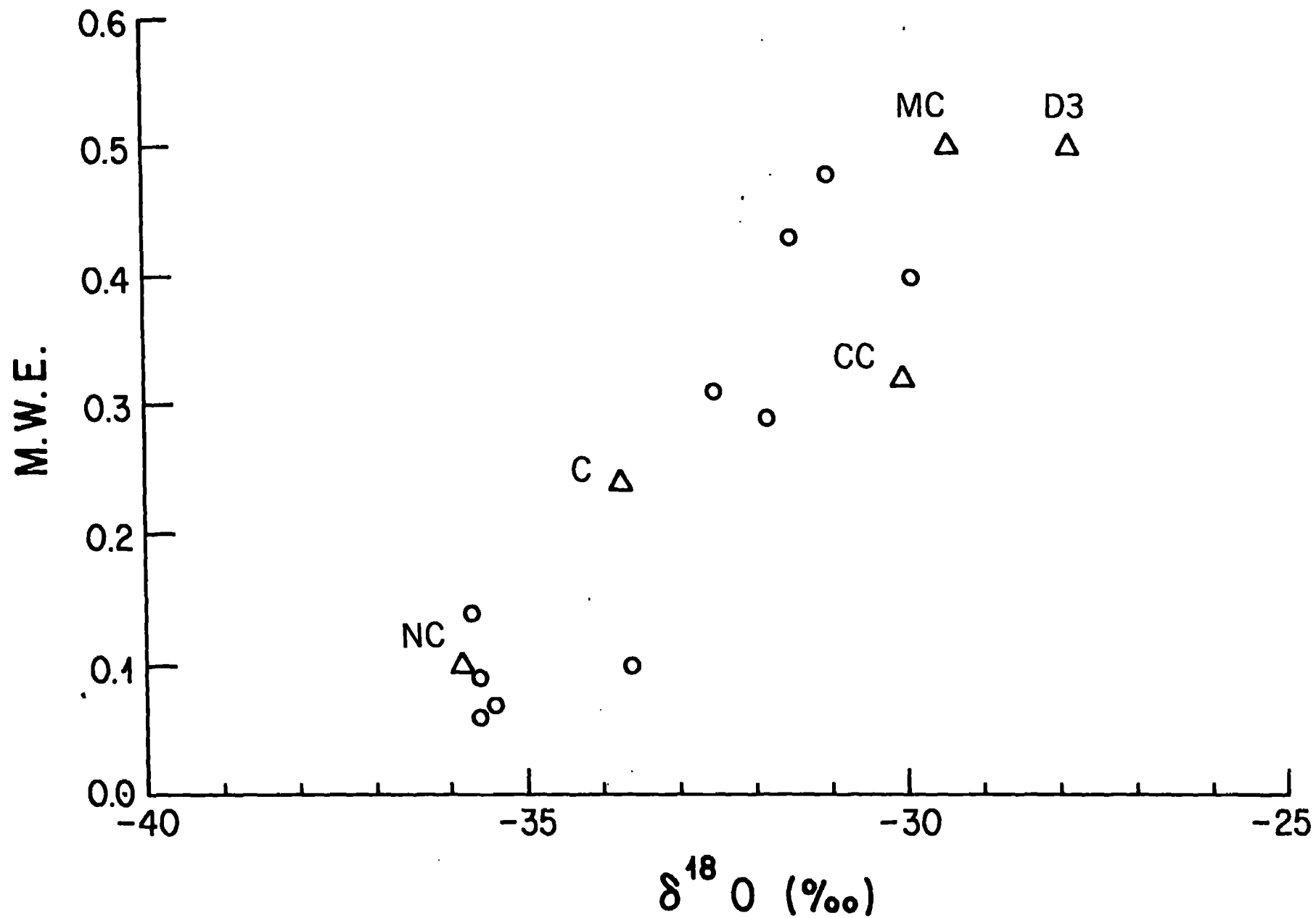


FIGURE 5.